

HOMOGENEOUS CATALYSTS IN HYPERSONIC COMBUSTION

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INTRODUCTION

Density and residence time both become unfavorably small for efficient combustion of hydrogen fuel in ramjet propulsion in air at high altitude and hypersonic speed. Raising the density and increasing the transit time of the air through the engine necessitates stronger contraction of the airflow area. This enhances the kinetic and thermodynamic tendency of H_2O to form completely, accompanied only by N_2 and any excess H_2 (or O_2). The by-products to be avoided are the energetically expensive fragment species H and/or O atoms and OH radicals, and residual (2H_2 plus O_2). However, excessive area contraction raises air temperature and consequent combustion-product temperature by adiabatic compression. This counteracts and ultimately overwhelms the thermodynamic benefit by which higher density favors the triatomic product, H_2O , over its monatomic and diatomic alternatives.

For static pressures in the neighborhood of 1 atm ($\times/\div 2.5$), static temperature must be kept or brought below ca. 2400 K for acceptable stability of H_2O . In contrast, temperatures exceeding ca. 3200 K at these static pressures actually give net endothermic pyrolysis of H_2 and O_2 , with more atoms than H_2O . Some relief from these limitations on efficient use of low-density air as an oxidant may be realized by expenditure of excess, initially cold fuel whose specific heat protects stability of H_2O and whose ejected mass contributes to thrust.

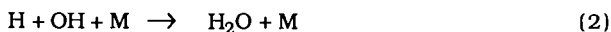
Another measure, whose requisite chemistry we address here, is to extract propulsive work from the combustion products early in the expansion. The objective is to lower the static temperature of the combustion stream enough for H_2O to become adequately stable before the exhaust flow is massively expanded and its composition "frozen." Prospective success of this measure in an acceptable expansion length is limited by the kinetics of the three-body "recombination" mechanism by which the composition of combustion products can shift exothermically.

We proceed to address this mechanism and its kinetics, and then examine prospects for enhancing its rate by homogeneous catalysts.

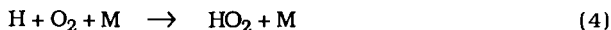
UNCATALYZED RECOMBINATION

Recombination Mechanism

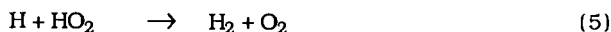
The most facile steps by which net recombination is understood to occur among the fragments of H_2O are:



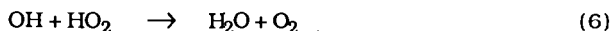
and the sequence



followed by

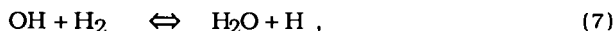


or



The respective exothermicities of steps (1) through (3), expressed as $-\Delta H$ in kcal/mole at zero Kelvin and rounded to the nearest whole number, are: 103, 118, and 101. The corresponding values [1] for steps (4) through (6) are: 49, 54, and 69. The net effects of the (4),(5) and (4),(6) sequences are indistinguishable from (1) and (2), respectively. For modeling, we use a more complete mechanism that includes alternate product channels of step (5) and a step analogous to (6) in which O-atom replaces OH. To set the stage here for the role of catalysts, we proceed without these other steps.

In compositions that are more or less hydrogen-rich, steps (1) and (2) contribute in parallel, in proportions governed by the H/OH ratio and the individual rate coefficients for each step with H_2O , N_2 , H_2 , and even atomic H as third bodies, collectively denoted M. The proportions of the products of steps (1) and (2) are subject to readjustment, with concomitant adjustment of the H/OH ratio. This occurs directly by the bimolecular step



whose exothermicity in the forward direction, as above, is only +15 kcal/mole, and whose forward and reverse rates are both large and become nearly equal. Both (1) and (2) are kinetically second order in the energetic fragments and so both rates diminish quadratically as net recombination is accomplished at fixed density, or as density is diminished by expansion. Up to ca. 2400 K at the densities for which their rates are significant, these steps are substantially irreversible, and their rate coefficients diminish only mildly with increasing temperature.

In stoichiometric and fuel-lean compositions, step (3) and the complex paths formed by steps (4), (5), and (6) are comparatively important, and step (1) not so. The reaction-order and irreversibility characteristics of step (3) are similar to those of steps (1) and (2)

discussed above. The thermochemistry of HO_2 makes reversibility of step (4) a serious complication. Within the (4) - (5)/(6) sequences, step (4) is rate-limiting at high fragment fractions and recombination is first-order in O_2 and H-atom populations. Although excess O_2 is not consumed in proportion to the fragments, progressive recombination diminishes the H-atom population nonlinearly. Reversible step (4) becomes equilibrated and step (6) becomes rate-limiting. And the net recombination rate by the (4)-(6) sequence becomes seriously diminished as temperature is raised above ca. 2000 K, leaving step (3) to become the dominant path near 2500 K in fuel-lean compositions and step (2) in near-stoichiometric compositions.

Hypersonic Flow Simulation

Earlier we [2] have modeled numerically the kinetics and thermomechanics of premixed, quasi-one dimensional, time-steady streamline segments that simulate supersonic H_2 /air combustion in a hypersonic ramjet. Of concern was the chemical basis of combustion efficiency. An undocumented Los Alamos code for finite-rate kinetics and thermochemistry, adapted to this application, was used.

Coupled engine/nozzle flow was simulated for a hypothetical vehicle flying at Mach 15 in air at 1.3×10^5 ft above the earth as a representative case. Stoichiometrically metered gaseous H_2 fuel from a lower temperature source was taken as mixed instantaneously with ram-compressed air at the initial station [3]. Static temperature and pressure of the mixed stream were 1463 K and 447 torr (59.5 kPa; 8.64 psia). Resulting internal axial stream velocity was 4.34×10^3 m/s.

For this base case, computed finite-rate reaction was followed through a 1-m long, constant-area combustor. Following ignition, near-equilibrium composition was reached at 2932 K, with 58% of the ideal combustion energy realized. Fragment species harbored the remaining 42%.

Next, expansion of the flow area beyond this 1-m station was modeled to an area sixteen times the combustor area over 1.5 m of further flow. Effects of selected area vs distance profiles were compared.

Computed static temperatures dropped from near 3000 K to near 1000 K. Computed composition began to shift toward a more complete energy-yield condition, but froze with only modest fractions of the remaining 42% realized.

This model scenario formed the base case for our present numerical examination of effects of added catalyst types in the early expansion.

CATALYZED RECOMBINATION

As potential catalysts for recombination, we may consider two classes:

- (a) Substances that catalyze steps (1)–(4) as third bodies, M, with large rate coefficients; and
- (b) Substances that introduce parallel paths analogous to the HO_2 sequence, (4)–(5)/(6), with such thermochemistry that, like O_2 , they are regenerated and not irreversibly consumed.

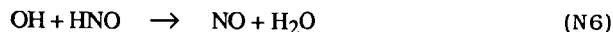
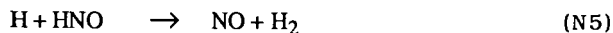
Such catalytic substances can enhance the energy recovery through recombination early in the expansion of combustion products in which ideal combustion is stoichiometrically incomplete owing to too high a temperature for the combustion-stream pressure. They can do so profitably if, in the time of such early expansion, they enable a greater yield of chemical energy and increment of streamline thrust to be achieved than could alternatively be achieved from the combined influences of more complete equilibrium combustion and uncatalyzed early recombination realized from addition of a like mass of excess fuel or "inert" thermal ballast to the combustion flow.

As prospective catalysts we select representative substances from those volatile materials that are known to inhibit flames. These are recognized by their qualitative consequences of lower flame speeds in gaseous systems that include them as additives, and/or wider minimum channel dimensions for flame propagation. Their mode of

action is generally associated with diminished radical populations in the ignition phase of combustion, where radicals (including the atomic species H and O) function as carriers in chain-reaction sequences. Paradoxically, the same agents and recombination mechanisms serve to promote the completion of combustion from an intermediate composition in which ignition coupled with high temperature have produced a surplus of "intermediate" fragments. Since experience teaches that reactions (1)–(4) have almost their largest rate coefficients with H₂O as the third body as with any known species, the flame-inhibiting catalysts we are led to consider come from class (b) above. Two chemical types of these catalysts are distinguished: (i) nonmetals, either as atoms or low-valence oxides, and (ii) molecular metal oxides.

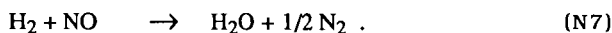
Nonmetal Oxide Catalyst

Nitric oxide, NO, is a prototype catalytic substrate to which H-atoms and also O-atoms and OH radicals each combine in a process analogous to step (4), and will be abstracted in steps analogous to (5)/(6). In each case the bond formed in the three-body step is analogous in strength to the bonds in the HO₂ from step (4). Thus, subsequent abstraction by a second atom or OH radical to form a 100–118 kcal/mole bond is exothermic, in the pattern of steps (5)/(6), and NO is liberated to complete a homogeneous catalytic cycle. The prototype steps for fuel-rich hydrogen-air recombination are:



The full set of steps used in modeling, and their rate coefficients, are conveniently surveyed elsewhere [4].

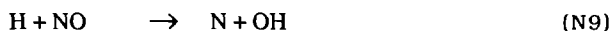
NO is not stable against atmospheric oxidation or physiologically benign enough to be a useful flame-retarding agent in room-temperature fire protection applications. Its role as a (generally undesirable) by-product of air-based combustion is well studied, however. Its presence in hypersonic propulsion streams is neither wholly avoidable nor dependent upon nonfuel material being carried in the vehicle for addition to the flow. Moreover, the behavior of NO as a recombination catalyst was directly studied early on [5,6] in postflame gases from premixed, fuel-rich, atmospheric pressure $\text{H}_2\text{-O}_2\text{-N}_2$ flat flames providing small, slowly decaying residual radical pools. In the 1600–2000 K temperature range so investigated, HNO is stable enough against dissociation that catalysis is pronounced. Recombination of the surplus fragments occurs unaccompanied by noticeable diminution of the artificially added ($[\text{NO}] + [\text{HNO}]$) inventory through thermodynamically spontaneous but slower global reaction



The catalytic behavior of NO in the hypersonic combustion situation we modeled differs from that in the flat flame in several respects, in consequence of (i) the higher combustion temperature ($2400 < T < 3000 \text{ K}$) we considered to precede expansion-induced recombination, and (ii) the significantly larger (forty-fold) fragment fraction (near 4% of the total flow, including N_2) to be recombined. The major effect is significant interruption of the catalytic cycle by frequent reversal of the bond-forming step (N4). The low net rate of (N4) becomes rate-limiting even as the larger H and OH populations make the HNO lifetime in steps (N5)/(N6) shorter than in the flat flame situation.

The second major difference, also primarily caused by the higher temperature range at which catalyzed recombination is needed in hypersonic combustion, is increased rates of the endothermic steps





of the extended Zeldovich chain. When that chain is completed by its rapid, exothermic step



there arises further need for recombination to accomplish reaction (N7).

Metal Oxide Catalysts

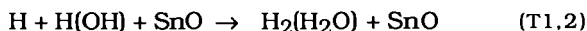
The other, and more promising class of recombination catalysts we have explored comprises partially oxidized forms of several metals, ranging in atomic weight from Mg to U. A survey was made [7] of twenty such metallic elements as part-per-million additives in atmospheric-pressure postflame gases near 1860 K. $\text{H}_2:\text{O}_2:\text{N}_2$ proportions were 3:1:6 and atom densities of $5 \times 10^{12} \text{ cm}^{-3}$ of each added metal were introduced as sprayed aqueous solution of a suitable salt. The largest catalytic effects [7], "2 orders of magnitude more effective than...NO...", occurred with the transition metals Cr, U, Sn and Mn. Similar catalysis also was found at 1860 K with the group II metals, Mg and the previously identified [8] heavier alkaline earths, Ca, Sr, and Ba. All these catalysts were further examined in hotter flames having lower proportions of N_2 , up to temperatures above 2400 K, where catalysis by the alkaline earth metals was significantly diminished. But, [7] "for Sn, Cr, and U [there was] no definite trend either up or down [over the 1800-2500 K range]." This finding implies that these metals will not lose their catalytic efficiency for promotion of recombination in the temperature regimes found in hypersonic ramjet propulsion.

For the group II elements and some if not all of the transition metals, catalytic sequences analogous to steps (4) - (6) are established.

In these, the analogs of O_2 and HO_2 are respectively, the strongly bound diatomic metal monoxide and the corresponding monohydroxide. Electronic states of the hydroxide other than its most strongly bound, ground state have been implicated in the catalytic sequence. Also, catalysis by involatile oxide particles is an incompletely resolved possibility for some of the transition metals, including Cr and U.

The flame chemistry and spectroscopy are more extensively studied [9] in the case of tin, and we chose this metal as the additive for modeling prospective catalyzed recombination in hypersonic combustion. In particular, SnO was shown to be the predominant species indistinguishable from 100% of the tin inventory. Even so, representation of the empirical catalysis by added Sn in postflame gases by means of elementary steps and their rate coefficients is uncertain.

Bulewicz and Padley [7] report an empirical rate constant, $k'_{\text{catalytic}}$ (k'_{cat}), for the global reactions



The k'_{cat} in this paper expresses the incremental contribution to the H-atom removal rate after subtraction of the terms from the uncatalyzed mechanism, representing the combined effect of steps (1) and (2) with H_2O , N_2 etc., as M. The rate coefficient was found to be

$$k'_{\text{cat}} \approx 5 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} .$$

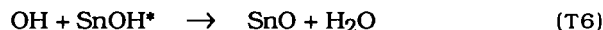
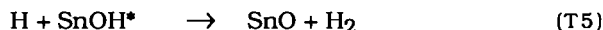
Allowance is included here for the stoichiometric factor of 2 between the rate of step (1) and the specific rate of reduction of the H-atom population. The mean of three k'_{cat} values above 2000 K is adopted. If the global reactions (T1,2) are assumed to be the elementary reaction steps for the catalytic mechanism a rate constant $k_{1,SnO}$ of this magnitude is unrealistically large.

Nevertheless, to assess the effectiveness of tin as a catalytic additive we incorporated into our kinetics model the reactions (T1,2).

With the addition of only 0.1% mole-fraction SnO of the total flow we realized an increase in the ideal combustion energy yield from the noncatalyzed 58% to 79%. This dramatic result compares to the equilibrium constrained result of nearly 100%.

The foregoing value of k'_{cat} is based on experience at $\leq 10^{-3}$ H-atom fraction in the flame gases, whereas early expansion of hypersonic combustion gases from a condition near 2900 K involved H-atom fraction up to 40 times larger. The consequent rate terms are thus extrapolated in our model to $\sim 10^3$ times larger magnitude. While this model indicated very strong catalysis its validity is uncertain.

As an alternative to using SnO as M in steps (1)-(4), the sequence:



has been postulated [7,9]. The superscript * denotes an electronically excited state of the monohydroxide molecule, SnOH.

Pursuing this catalytic sequence, steps (T4)-(T6) to represent the k'_{cat} in Ref. 7 paper, the deduced the equilibrium-constant ratio was

$$K_4 \equiv k_{\text{T4}}/k_{-\text{T4}} = 3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$$

and the rate coefficient was

$$k_{\text{T5}} \approx 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

When we have estimated individual values of $k_{T_4,M}$ and $k_{T_4,M}$ for H_2O and N_2 , and M we find catalytic rates under hypersonic combustion conditions that are understandably smaller than by the k'_{cat} above, but not insignificant.

CONCLUSION

The more complete existing information on nonmetal oxides indicates that catalytic enhancement of combustion power by adding intentionally these materials will be unattractive, but the effects of constituents such as NO formed naturally from combustion in air are not negligible. However, the effects we predict based on the available literature data on metal oxides is encouraging. We conclude that further experimental investigation of volatile metallic additives as catalysts for recombination of H_2O fragments at high temperature, $T > 2400$ K, is advisable to advance the prospect of efficient, kinetically controlled enhancement of power for propulsion of hypersonic ramjets in circumstances where combustion would otherwise be thermochemically complete.

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